

We claim:

1. A process for increasing the yield in preparing polyhydric alcohols, in particular trimethylolpropane, obtained by condensing formaldehyde with a higher aldehyde, by acid treatment of a mixture (high boiler fraction) comprising derivatives of these alcohols obtained by workup and having a higher boiling point than the particular alcohol and recovery of the polyhydric alcohol from the acid-treated high boiler fraction, wherein the water content of the high boiler fraction is from 20 to 90% by weight, based on the total amount of high boiler fraction and water.
- 15 2. A process as claimed in claim 1, wherein the polyhydric alcohol has been prepared by aldolizing formaldehyde with a higher aldehyde in the presence of catalytic amounts of a tertiary amine and hydrogenating the mono- or polymethylolalkanals obtained in this way, preferably of dimethylolbutanal to trimethylolpropane.
3. A process as claimed in claim 2, which comprises the following steps:
  - 25 a) distillative removal of the components having lower boiling points than the polyhydric alcohol from the crude product of the hydrogenation of the mono- or polymethylolalkanals
  - 30 b) separation of the resulting bottom product in a second distillation stage into a high boiler fraction and a fraction comprising the majority of the polyhydric alcohol
  - 35 c) acid treatment of the high boiler fraction
  - d) distillation of the fraction comprising the majority of the polyhydric alcohol to remove the more volatile compounds (medium boiler fraction) and recovery of pure polyhydric alcohol

40 wherein the acid-treated high boiler fraction is recycled into the hydrogenation of the mono- or polymethylolalkanals to the polyhydric alcohol.

4. A process as claimed in claim 3, wherein some or all of the medium boiler fraction removed from the fraction comprising the majority of the polyhydric alcohol by distillation is mixed with the high boiler fraction before the acid treatment.
5. A process as claimed in any of claims 1 to 4, wherein the acid concentration is from 0.1% by weight to 20% by weight, based on the total amount of high boiler fraction or the mixture of high boiler fraction and middle boiler fraction and water.
10. A process as claimed in any of claims 1 to 5, wherein the acid is selected from C<sub>1</sub>- to C<sub>12</sub>-carboxylic acids, C<sub>2</sub>- to C<sub>12</sub>-dicarboxylic acids, sulfonic acids, mineral acids, carbon dioxide, sulfur dioxide and acidic ion exchangers.
15. A process as claimed in any of claims 1 to 6, wherein formic acid is used.
20. A process as claimed in any of claims 1 to 7, wherein the polyhydric alcohols are selected from the group of trimethylolethane, trimethylolpropane, trimethylolbutane, neopentyl glycol and pentaerythritol.
25. A process as claimed in any of claims 1 to 8, wherein the polyhydric alcohol is trimethylolpropane.

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